PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-242817
(43)Date of publication of application : 19.09.1995

(51)Int.Cl. C08L 77/00
C08K 3/34
C08K 5/3477
C08K 13/04

(21)Application number : 06-059896
(22)Date of filing : 04.03.1994

(71)Applicant : SHOWA DENKO KK
(72)Inventor : TAKEDA TADASHI
KIRIKOSHI HIROSHI

(54) POLYAMIDE RESIN COMPOSITION

(57)Abstract:
PURPOSE: To obtain a polyamide resin composition, capable of holding high flame retardancy, improved in mold deposit, foaming and bleedout phenomena and useful as electronic and electrical apparatuses, etc., by blending a polyamide resin with a layered clay mineral in which a specific flame retardant is coordinated between layers.
CONSTITUTION: This composition comprises (A) a polyamide resin and (B) a layered clay mineral in which melamine is coordinated between layers and/or (C) a layered clay mineral in which cyanuric acid is coordinated between layers. Furthermore, 100 pts.wt component (A) is preferably blended with the components (B) and (C) in an amount of 1-20 pts.wt. in total of both and the content of the melamine which is a 6-membered cyclic compound of 2,4,6-triamino-1,3,5-triazine in the component (B) is preferably 0.01-40wt.%. The content of the cyanuric acid that is a 6-member cyclic compound of 2,4,6- trihydroxy-1,3,5-triazine in the component (C) is preferably 0.01-40wt.%.

CLAIMS

[Claim(s)]
[Claim 1](A) A polyamide resin composition which consists of layer argillite which made a laminar clay mineral and/or (C) cyanuric acid which made polyamide resin and (B) melamine configurate between layers configurate between layers.
[Claim 2](A) The polyamide resin composition according to claim 1 which carries out 1-20 weight-section combination by making the (B) ingredient and/or the (C) ingredient into the total quantity to ingredient 100 weight section.
[Claim 3](B) The polyamide resin composition according to claim 1 or 2 melamine content in an ingredient and whose cyanuric acid content in the (C) ingredient are 0.01 to 40 % of the weight

respectively.

[Translation done.]

* NOTICES *

JPO and INPIT are not responsible for any
damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the polyamide resin composition which has high fire retardancy and in which a mold deposit, foaming, and a bleeding phenomenon were improved.
[0002]
[Description of the Prior Art]Generally polyamide resin is excellent in various characteristics, such as a mechanical strength, heat resistance, an electrical property, and a frictional wearing characteristic, and is used for a wide range of fields, such as a machine part, autoparts, electrical and electric equipment, electronic machine parts, as engineering plastics. In recent years, as for the use, surface characteristics, such as gloss, have come to be thought as important from a point of the field of building materials, office furniture, an automotive interior material, etc., and commodity value. In particular, since polyamide resin itself is self-extinguishing, it is suitably used for electrical-part material.
[0003]There are not few cases where the demand of flameproofing of a plastic material becomes severe and still more advanced flameproofing is needed also in polyamide resin in an electronic electric appliance use on the other hand in recent years. Then, giving high fire retardancy which passes safety standard UL-94V-0 of U.S. Underwriters Laboratories, for example is examined, without spoiling the original performance of polyamide resin. For example, addition of the following fire retardant is proposed.
a) Melamine compound (for example, JP,47-41745,B)
b) Cyanuric acid system compound (for example, JP,50-105744,A)
c) This mol addition of melamine and cyanuric acid (for example, JP,53-31759,A)
[0004]However, in the above-mentioned method, when a making machine was operated for a long time, there were problems that sublimate adhered to foaming, an appearance defect, or the metallic mold surface by decomposition of fire retardant in stagnation resin, such as a mold depository jet phenomenon. The phenomenon in which fire retardant carries out bleed out by what is called annealing treatment of heat-treating mold goods happens, and there is also a possibility of becoming a cause of the contact fault of an electronic electrical part.
[0005]
[Problem(s) to be Solved by the Invention]This invention is made in view of this situation, and is a thing.
The purpose is to provide the polyamide resin composition which it held [polyamide resin composition] and had a mold deposit, foaming, and a grido out phenomenon improved.

[0006]
[Means for Solving the Problem]As a result of repeating research for **** on the above-

mentioned problem wholeheartedly, by blending a laminar clay mineral which made fire retardant configurate between layers, this invention persons find out that the above-mentioned purpose can be attained, and came to complete this invention based on this knowledge.
[0007]That is, this invention provides a polyamide resin composition which consists of layer argillite which made a laminar clay mineral and/or (C) cyanuric acid which made (A) polyamide resin and (B) melamine configurate between layers configurate between layers. This invention is explained concretely below.
[0008](A) polyamide resin in this invention is a high molecular compound which has an acid amide (-CONH-) in a repeating unit. The polyamide specifically obtained from dicarboxylic acid and diamine, such as the polylactam; polyamide 66, such as the polyamide 6, the polyamide 11, and the polyamide 12, the polyamide 610, the polyamide 612, and the polyamide 46; The polyamide 6-66, the polyamide 6-12, Copolymer polyamide, such as polyamide 6-66-610; Polyamide 6-6T (T: terephthalic acid component), And the semi aromatic polyamide obtained from aromatic dicarboxylic acid, meta=xylylene diamine, or alicycle fellows diamine, such as isophthalic acid; polyester amide, polyether amide, polyester ether amide, etc. are mentioned. These polyamide resin may be used independently and may use two or more sorts together. These polyamide resin is not restricted to a kind or concentration of the end group.
[0009]In this invention, a laminar clay mineral which made a laminar clay mineral and/or (C) cyanuric acid which made (A) polyamide resin configurate (B) melamine between layers configurate between layers is blended. A laminar clay mineral used for this invention has the character to expand with water and/or an organic matter, and when swelling it, it says silicate in which interlaminar distance (monotonous centroid distance of a laminar clay mineral is said) will be 15 A or more. In this case, in order that water and/or an organic matter may break into a position between layers of a crystal of a laminar clay mineral and may push between layers open, the whole crystal swells. Melamine or cyanuric acid breaks into a position between layers of a crystal of a laminar clay mineral, and coordination between layers in this invention means the state where arranged regularly and a middle crystallized state of an organic matter and an inorganic substance was formed between layers.
[0010]They are mentioned by stratified phyllo silicic acid mineral etc. which comprise a magnesium silicate or aluminum silicate as a laminar clay mineral, and specifically, Smectite system argillite and BAMYU lights, such as synthetic mica, talc, montmorillonite, saponite, beidellite, nontronite, hectorite, and a stevensite, Huy Rosa Ito, etc. are mentioned. Synthetic mica, montmorillonite, and a smectite are preferred also in these. As for 6-20 A and a length of one side, about 0.002-1 mm is [thickness of a layer of a laminar clay mineral in this invention] preferred.
[0011]Melamine in this invention is 2, 4, and 6-triamino 1,3,5-triazine. It is a compound of the shape of 6 membered-rings of [$(CNH_2)_3N_3$], and has with specific gravity 1.57 (40 **) and a melting point of 350 ** description as the crystal of a white monoclinic system. This melamine is used as a raw material of this melamine resin. Cyanuric acid in this invention is 2,4,6-Tori oxy-1,3,5-triazine. It is a compound of the shape of 6 membered-rings of [$(COH)_3N_3$], and has the melting point of not less than 360 ** as the crystal of a colorless columnar crystal. melamine and cyanuric acid which are used by this invention -- a commercial item -- as it is -- or it can be ground and used -- it carries out and some of amino groups or hydroxyl groups may be replaced by other substituents.
[0012]In order to make a laminar clay mineral configurate melamine or cyanuric acid between layers, it is required to process melamine or cyanuric acid with a laminar clay mineral underwater. That is, after making it dissolve, agitating melamine or cyanuric acid underwater, layer coordination processing is performed for churning continuously [it adds agitating a laminar clay mineral and / 60 ** / for about 24 hours]. A laminar clay mineral which melamine or cyanuric acid configurated between layers is obtained by [the] carrying out a back fault and carrying out vacuum drying.
[0013]Coordination between layers is performed so that melamine in a laminar clay mineral which melamine or cyanuric acid obtained eventually configurated between layers, or quantity of

cyanuric acid may be 0.1 to 25% of the weight preferably 0.01 to 40% of the weight. If an effect of fire retardancy [quantity / of melamine or cyanuric acid] in less than 0.01 % of the weight cannot be demonstrated and it exceeds 40 % of the weight, depressor effect of foaming, mold DEPOJIETTO, and bleed out will not show up.
[0014](B) loadings of a laminar clay mineral which made a laminar clay mineral and/or (C) cyanuric acid which made melamine configurate between layers configurate between layers -- per (A) polyamide resin 100 weight section -- as the total quantity -- usually -- it is 3 - 15 weight section especially preferably two to 18 weight section preferably one to 20 weight section. Loadings become insufficient [less than one weight section / fire retardancy]. On the other hand, since a mechanical strength will fall if 20 weight sections are exceeded, it is not desirable.
[0015]Restriction in particular does not have a method of mixing and kneading polyamide resin of this invention, and a laminar clay mineral configurated between layers, and using as a resin pellet, and it should just adopt a method currently generally performed in the synthetic resin field. As a mixing method, a method of making a resin mixture which carried out the dry blend knead by a molten state using kneading machines, such as a screw-type extrusion machine, etc. are mentioned using mixers, such as a Henschel mixer, a tumbler, and a ribbon blender. To a constituent of this invention, a conventional additive agent, for example, a plasticizer, various stabilizer, a spray for preventing static electricity, a reinforcing agent, a paint, paints, various bulking agents, etc. may be added by request.
[0016]
[Example]Hereafter, an example explains this invention in more detail. The performance testing method applied to the next correspondingly.
[A fire-resistant examination] Injection molding of the specimen (5 inches in length, 1/2 inch in width, and 1/3 inch in thickness) was carried out, and it tested according to safety standard UL-94 of the U.S.
[0017][Measurement of the amount of mold deposits] The affix of the parting line of after 300-piece shaping and a metallic mold was extracted for the plate using the injection molding machine of 50 t of the maximum clamping pressure, and weighing of the quantity was carried out.

[0018][Bleed out sex test] The above-mentioned plate fabricated to measurement of the amount of mold TEPOJITTO was neglected in the constant temperature/humidity chamber of 40 ** and 95%RH for 500 hours, the bleed out nature on the surface of a plate was observed by viewing, and it judged on the following standard.
O : -- completely -- nothing **: -- x: seen somewhat -- remarkable [0019][Fizz examination] The plate was fabricated in molding-cycle-time 15 seconds, 30 seconds, and 60 seconds, foaming of the plane surface was observed by viewing, and it judged on the following standard.
O : cycle time at least 60 seconds do not have foaming.
**: Foaming is seen in cycle time 30 seconds.
x: Foaming is seen in cycle time 15 seconds.
[0020]Examples 1-4 [Manufacture of the laminar clay mineral made to configurate between layers] After making it dissolve, agitating melamine or cyanuric acid 1 weight section to water 100 60 ** weight section, it added agitating laminar clay mineral 3 weight section, churning was continued at 60 ** for about 24 hours, and layer coordination processing was performed. Then, the laminar clay mineral which made melamine or cyanuric acid configurate between layers was obtained by filtering, removing water and carrying out vacuum drying at 80 ** for two days. Cable address M-M, C-M, and M-S show the laminar clay mineral made to configurate between layers with obtained melamine or cyanuric acid. The presentation of these cable addresses is as in Table 1.
[0021]
[Table 1]

表1

層間配位処理された層状粘土鉱物略号	層状粘土鉱物の種類	メラミン含量（重量 %）	シアヌル含量、（重量%）
M－M	モンモリロナイト	２５	－
C－M	モンモリロナイト	－	２５
M－S	スメクタイト	２５	－

[0022][Manufacture of a polyamide resin composition] After carrying out preliminary mixing of the laminar clay mineral (Ikegai Corp. PCM-30) 10 weight section which polyamide 66 pellet 100 weight section of relative viscosity (the 1-% of the weight polymer solution in 98% sulfuric acid is measured at 25 **) 1.3 was made to configurate between the layers of the presentation shown in Table 2 with a tumbler, Melt kneading was supplied and carried out to the 30 mmphi said direction biaxial extrusion machine, and it pelletized by the cutter after water cooling. Thus, using the pellet of this obtained polyamide resin composition, injection molding was performed, the specimen and the plate (100 mm x 100 mm, and 2 mm in thickness) were created, and evaluation of fire retardancy, the amount of mold deposits, and bleed out was performed.
[0023]At the one to comparative example 3 comparative example 1, it is the polyamide 66. 100 weight sections, montmorillonite 7.5 weight section, About melamine 2.5 weight section, it is the polyamide 66 at the comparative example 2. Again 100 weight sections, mono- MORIRO night 7.5 weight section, and cyanuric acid 2.5 weight section in the comparative example 3. polyamide 66 100 weight sections -- melamine and a cyanuric acid this mol reactant -- each After carrying out preliminary mixing with a tumbler, melt kneading was supplied and carried out to the 30 mmphi said direction biaxial extruder, and it pelletized by the cutter after water cooling. Injection molding was performed using the obtained pellet, the specimen and the collar plate were created, and it evaluated like the example. The evaluation test result was shown in Table 2.
[0024]
[Table 2]

表２

実施例又比較例	ポリアミド樹脂組成物							性能評価			
	ポリアミド樹脂	層間配位させた層状粘土鉱物			メラミン	シアヌル酸	未処理モンモリロナイト	難燃性	発泡状態	モールドデポジット量	ブリードアウト性
		M-M	C-M	M-S							
	（重量部）	（重量部）	（重量部）	（重量部）	（重量部）	（重量部）	（重量部）			（mg）	
実施例１	100	10	－	－	－	－	－	V－0	○	0.4	○
２	100	－	10	－	－	－	－	V－0	○	0.4	○
３	100	5	5	－	－	－	－	V－0	○	0.4	○
４	100	－	－	10	－	－	－	V－0	○	0.4	○
比較例１	100	－	－	－	2.5	－	7.5	V－0	△	5.9	×
２	100	－	－	－	－	2.5	7.5	V－0	△	5.9	△
３	100	－	－	－	2.5	2.5	－	V－0	×	10.2	×

[0025]The following thing can be said from Examples 1-4 and the comparative examples 1-3.
** In Examples 1-4, fire retardancy, fizz, and bleed out nature are good, and there are also few amounts of mold deposits.
** Although fire retardancy is held in the comparative examples 1-3 which do not use the laminar clay mineral made to configurate between layers, fizz and bleed out nature are inferior, and there are also many amounts of mold deposits.
[0026]
[Effect of the Invention]Since a mold deposit phenomenon and a foaming phenomenon are remarkably improved by using the polyamide resin composition in this invention, Mold goods holding advanced fire retardancy, while it has the outstanding high cycle nature, since a bleed out phenomenon is improved remarkably, high-humidity/temperature-izing of industrial value is also very large.

[Translation done.]

WRITTEN AMENDMENT

---------- [Written amendment]
[Filing date]April 8, Heisei 6
[Amendment 1]
[Document to be Amended]Specification
[Item(s) to be Amended]Claim 1
[Method of Amendment]Change
[Proposed Amendment]
[Claim 1](A) A polyamide resin composition which consists of a laminar clay mineral which made a laminar clay mineral and/or (C) cyanuric acid which made polyamide resin and (B) melamine configurate between layers configurate between layers.
[The amendment 2]
[Document to be Amended]Specification
[Item(s) to be Amended]0007
[Method of Amendment]Change
[Proposed Amendment]
[0007]That is, this invention provides the polyamide resin composition which consists of a laminar clay mineral which made the laminar clay mineral and/or (C) cyanuric acid which made (A) polyamide resin and (B) melamine configurate between layers configurate between layers.
This invention is explained concretely below.

[Translation done.]